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**EP 0 482 817 B1**

## Description

The present invention relates to a method for preparing a highly active catalyst for hydrogenation of a hydrocarbon oil, which satisfies the requirement of reducing the sulphur content in a light oil.

5 In hydrogenation of a hydrocarbon oil in the presence of hydrogen for hydrogen addition, desulphurization, denitrogenation, decomposition or the like, a hydrogenating catalyst (hereinafter referred to as a "catalyst") composed of a catalyst carrier of a porous inorganic oxide, such as alumina, titania or silica, and active metal components of the Group VI of the Periodic Table of Mo or W and the Group VIII of the same of Ni or Co, as carried on the carrier, is used as a basical catalyst. In the catalyst of the type, in general, the  
10 above-mentioned active metals as carried on the catalyst carrier are in the form of their oxides. Since such metal oxides are inactive as they are, the catalyst with such metal oxide could not be applied to hydrogenation. Therefore, the metal oxides are necessarily activated by converting them into the corresponding metal sulphides. Under the situation, after the above-mentioned catalyst has been filled in a device for hydrogenation of a hydrocarbon oil, an adequate pre-sulphurization treatment is indispensable in  
15 which the catalyst layer in the device is necessarily sulphurized by introducing a hydrocarbon oil containing a sulfurizing agent as dissolved therein therethrough under heat. It is known that the active site of the thus pretreated catalyst is formed on the surfaces of the resulting active metal sulfides so that the total number of the active sites would increase with increase of the exposed surface area of the active metal sulfides to yield, as a result, a high catalyst activity. Increase of the exposed surface area of the active metal sulfides  
20 may be attained by enhanced dispersion of the active metal sulfides as carried on the catalyst carrier or by minimization of the crystal size of the respective active metal sulfides. Method of preparing a catalyst having fine crystals of active metal sulfides as finely dispersed and carried on a carrier have been disclosed. For instance, Japanese Patent Application Laid-Open Nos. 59-102442 and 59-69147 mention a series of a method of preparing a catalyst in which a catalyst carrier such as an alumina is dipped in an  
25 aqueous solution of active metals containing a carboxylic acid, such as citric acid or malic acid, as a complexing agent for active metals and thereafter it is fired. EP 0181035(A2) mentions a method of preparing a catalyst in which an organic compound having a nitrogen-containing ligand (e.g., amino group, cyano group) such as nitriloacetic acid, ethylenediaminetetraacetic acid or diethylenetriamine is used as a complexing agent and is added to an aqueous solution of active metals, a catalyst carrier such as an  
30 alumina or silica is dipped in the resulting aqueous solution of active metals, and the catalyst composed of active metals as carried on the catalyst carrier is then dried at a temperature of not higher than 200 °C without firing.

In accordance with the method of adding a carboxylic acid as a complexing agent followed by firing, the carboxylic acid added is effective for elevating the stability of the active metal-dipping solution as it acts as  
35 a complexing agent for active metals and additionally the acid is also effective for inhibiting coagulation of active metals. In the method, however, the active metals would finally coagulate because of the final firing step so that the finally obtained catalyst by the method could not have a sufficiently improved catalyst activity. The method is defective in this point. On the other hand, in accordance with the method as disclosed in EP 0181035(A2), since the active metal ions such as Mo or Ni ions are firmly coordinated with  
40 the nitrogen-containing compound, such ions are carried on the carrier in the form of a highly dispersed condition. In addition, since the catalyst with the carrier is not calcined but is merely dried at a low temperature of not higher than 200 °C, the dispersion of the active metals is finally maintained as it is. Further, since the active metal ions are directly formed into sulfides thereof without forming oxides thereof by pre-sulphurization, the finally obtained catalyst may have an extremely highly dispersed state. Because of  
45 the reasons, the catalyst prepared by the method has a higher activity than any other conventional catalysts, but it could not still have a high hydrogenation and desulfurization activity enough to meet the recent demand of reducing the sulfur content in a light oil (precisely, to 0.05 % by weight or less as the sulfur content in a light oil) for solving the problem resulting from the current legal controls on gaseous wastes. Additionally, since the catalyst contains a nitrogen-containing organic compound such as  
50 nitriloacetic acid or the like, there is a problem that the organic compound would be decomposed in the pre-sulphurization step to generate a toxic gas such as hydrogen cyanide.

The object of the present invention is to provide a method of preparing a highly active catalyst which may satisfy the above-mentioned requirement of reducing the sulphur content in a light oil.

55 The present inventor repeatedly studied for the purpose of solving the above-mentioned problems in the prior arts and of attaining the above-mentioned object, and, as a result, has found that the object can be attained by adding a determined amount of a hydroxycarboxylic acid to a catalyst composed of base metals and optionally phosphoric acid as carried on a carrier followed by drying the resulting catalyst at a temperature not higher than 200 °C prior to loading onto a reactor. On the basis of the finding, the inventor

has achieved the present invention.

Specifically, in accordance with the first embodiment of the present invention, there is provided a method of preparing a catalyst for hydrogenation of a hydrocarbon oil, in which a hydroxycarboxylic acid is added to a catalyst carrying a metal of the Group VI of the Periodic Table and a metal of Group VIII of the same on a carrier in an amount of from 0.3 to 5 molar times of the total metal molar number of the metal of the Group VI and the metal of the Group VIII, and thereafter the resulting catalyst is dried at a temperature not higher than 200 °C prior to loading onto a reactor.

In accordance with the second embodiment of the present invention, there is provided a method of preparing a catalyst for hydrogenation of a hydrocarbon oil, in which a hydroxycarboxylic acid is added to a catalyst carrying a metal of the Group VI of the Periodic Table and a metal of the Group VIII of the same along with phosphoric acid on a carrier in an amount of from 0.3 to 5 molar times of the total metal molar number of the metal of the Group VI and the metal of the Group VIII, and thereafter the resulting catalyst is dried at a temperature not higher than 200 °C prior to loading onto a reactor.

In the present invention, at least one selected from ordinary porous substances, such as alumina, silica, titania, zirconia, active charcoal and the like, is used as a catalyst carrier substance in a convention manner.

As the metal of the Group VI of the Periodic Table, at least one of Mo and W is used; and as the metal of the Group VIII of the same, at least one of Co and Ni is used.

As examples of a hydroxycarboxylic acid is usable as a complexing agent in the present invention, there are mentioned, for example, glycolic acid, hydroxypropionic acid, hydroxybutyric acid, hydroxyhexanoic acid, tartaric acid, malic acid, glyceric acid, citric acid, gluconic acid, etc.

As phosphoric acid, anyone of metaphosphoric acid, pyrophosphoric acid, orthophosphoric acid, triphosphoric acid and tetraphosphoric acid can be used. A soluble salt of the acid such as nickel phosphate may also be used.

The amount of the metal of Mo or W of the Group VI of the Periodic Table to be carried on the carrier is desirably from 5 to 30 % by weight as its oxide. The amount of the metal of Ni or Co of the Group VIII of the same to be carried on the carrier is desirably from 1 to 8 % by weight as its oxide. If the amounts of such active metals to be carried on the carrier are less than those falling within the above-mentioned ranges, a highly active catalyst could not be obtained by the method of the present invention. On the other hand, if they are more than those falling within the above-mentioned ranges, the pores of the carrier would be clogged with the active metals so that internal diffusion of a hydrocarbon oil in the catalyst would be inhibited and the activity of the catalyst would be poor.

Phosphoric acid is desired to be added to the catalyst in an amount of from 0.1 to 8 % by weight as  $P_2O_5$ , whereby the activity of the catalyst is elevated further.

The hydroxycarboxylic acid is added to the catalyst having metals of the Group VI and the Group VIII of the Periodic Table as carried on a carrier or to the catalyst having the metals along with phosphoric acid as carried on a carrier, and the amount of the hydroxycarboxylic acid to be added is from 0.3 to 5 molar times of the total molar number of the metals of the Group VI and the Group VIII. If the amount of the acid added is less than 0.3 molar time, it would be insufficient for coordinating and complexing the active metals. If, however, the amount of the acid added is more than 5 molar times, a carbonaceous material would remain or precipitate in the catalyst to inhibit sulfurization of the active metals. Anyway, the both are disadvantageous as lowering the catalyst activity.

The drying temperature of drying the catalyst is not higher than 200 °C. This is because, if the temperature is higher than 200 °C, the added complexing agent would disadvantageously decompose.

The catalyst of the present invention thus prepared under the above-mentioned conditions is in the form of a coordination compound composed of the active metal ions of Mo, W, Ni and/or Co ions and the added hydroxycarboxylic acid. The coordination compound is stabilized and carried on the catalyst carrier. Though not clear, the reason why the activity of the catalyst as obtained by the use of a hydroxycarboxylic acid as a complexing agent is much higher than any other conventional catalyst as prepared by the use of a nitrogen-containing compound such as nitriloacetic acid, ethylenediaminetetraacetic acid or diethylenetriamine as a complexing agent could be considered because the decomposition behavior of the respective complexing agents would have some relation to the decomposing property of active metal sulfides since hydroxycarboxylic acids and nitrogen-containing organic compounds differ from each other in the decomposition behaviors thereof.

Next, the present invention will be explained in more detail by way of the following examples, which, however, are not intended to restrict the scope of the present invention.

**EXAMPLE 1**

800 ml of an aqueous solution of active metals, as prepared from 193 g of molybdenum trioxide, 82 g of cobalt carbonate, 61.5 g of 85 % phosphoric acid and water, was infiltrated into one kg of  $\gamma$ -alumina carrier having a specific surface area of 280 m<sup>2</sup>/g and a pore capacity of 0.75 ml/g, and the thus infiltrated  $\gamma$ -alumina carrier was dried at 110 °C for 5 hours. Next, 152.1 g of glyceric acid was infiltrated into 250 g of the dried product, which was then further dried at 110 °C for 10 hours to obtain a catalyst sample (Catalyst-A). Regarding the active metal contents in Catalyst-A, Mo content therein was 15 % by weight as MoO<sub>3</sub>, Co content therein was 4 % by weight as CoO, and P content therein was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of the glyceric acid added was 2.5 molar times of the total molar number of Mo and Co. As an activity test of Catalyst-A thus obtained, a Kuwait normal pressure light oil having the following properties was subjected to hydrogenation and desulfurization with Catalyst-A.

|                                 |       |
|---------------------------------|-------|
| Specific gravity (15/4 °C)      | 0.844 |
| Sulfur content (wt %)           | 1.55  |
| Distillation property           |       |
| Initial distillation point (°C) | 231   |
| 50 vol.% point (°C)             | 313   |
| Final point (°C)                | 390   |

The reaction was effected under the conditions mentioned below, using a flow reactor system.

|  |     |
|--|-----|
| Amount of catalyst (ml)                                | 15  |
| Liquid space velocity of crude oil (hr <sup>-1</sup> ) | 2   |
| Hydrogen pressure for reaction (kg/cm <sup>2</sup> G)  | 30  |
| Reaction temperature (°C)                              | 330 |
| Ratio of hydrogen/oil flow (Nl/l)                      | 300 |
| Oil flow period (hr)                                   | 88  |

A rate constant of the catalyst sample (Catalyst-A) is calculated out as the desulfurization rate is considered to be proportional to the 1.75th power of the sulfur content in the oil after the treatment, and a relative rate constant of Catalyst-A is obtained on the basis of Catalyst-Q (Comparative Example 4 which will be mentioned below) having a standard rate constant of 100. It is shown in the Table mentioned below along with the desulfurization percentage (%) of the crude oil with Catalyst-A.

**EXAMPLES 2 TO 5**

Catalysts-B, C, D and E were prepared in the same manner as in Example 1, except that 101.3 g of glycolic acid (Example 2), 94.8 g of lactic acid (Example 3), 99.0 g of  $\alpha$ -hydroxybutyric acid (Example 4) and 125.5 g of  $\alpha$ -hydroxyhexanoic acid (Example 5) were used, respectively, as a complexing agent. Regarding the active metal contents in these catalysts, Mo content was 15 % by weight as MoO<sub>3</sub>, Co content was 4 % by weight as CoO and P content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of the complexing agent in these catalysts was 2.5 molar times of the total molar number of Mo and Co. The activity test of these catalysts was effected in the same manner as in Example 1, and the results obtained are shown in the Table below.

**EXAMPLES 6 TO 8**

400 ml of an aqueous solution of active metals, as prepared from 96.2 g of molybdenum trioxide, 41 g of cobalt carbonate, 30.8 g of 85 % phosphoric acid and water, was infiltrated into 500 g of the above-mentioned  $\gamma$ -alumina carrier, which was then dried at 110 °C. Next, 56.0 g of tartaric acid (Example 6), 50.5 g of malic acid (Example 7) or 132.6 g of gluconic acid (Example 8) was infiltrated into 200 g of the dried product, which was dried at 110 °C for 10 hours. Accordingly, Catalyst-F, G and H were obtained, respectively. Regarding the active metal contents in these catalysts, Mo content was 15 % by weight as MoO<sub>3</sub>, Co content was 4 % by weight as CoO and P content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of

the tartaric acid or malic acid added was 1.25 molar times of the total molar number of Mo and Co; and that of the gluconic acid added was 1.1 molar times of the same. The activity test of these catalysts was effected in the same manner as in Example 1, and the results obtained are shown in the Table below.

#### 5 EXAMPLE 9

160 ml of an aqueous solution of active metals, as prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate, 12.3 g of 85 % phosphoric acid and water, was infiltrated into 200 g of the above-mentioned  $\gamma$ -alumina carrier, which was then dried at 110°C for 5 hours. Next, 67.0 g of citric acid was  
 10 infiltrated into the dried product, which was again dried at 110°C for 10 hours. Thus, a catalyst sample (Catalyst-I) was obtained. Regarding the active metal contents in Catalyst-I, Mo content was 15 % by weight as  $\text{MoO}_3$  and Co content was 4 % by weight as CoO. The amount of the citric acid added was 0.8 molar time of the total molar number of Mo and Co. The activity test of the catalyst was effected in the same manner as in Example 1, and the results obtained are shown in the Table below.

#### 15 EXAMPLE 10

160 ml of an aqueous solution of active metals, as prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate, 12.3 g of 85 % phosphoric acid, 67.0 g of citric acid and water, was infiltrated into 200  
 20 g of the above-mentioned  $\gamma$ -alumina carrier, which was then dried at 110°C for 5 hours. Thus, a catalyst sample (Catalyst-J) was obtained. Regarding the active metal contents in Catalyst-J, Mo content was 15 % by weight as  $\text{MoO}_3$ , Co content was 4 % by weight as CoO and P content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of the citric acid added was 0.8 molar time of the total molar number of Mo and Co. The activity test of the catalyst was effected in the same manner as in Example 1, and the results obtained are  
 25 shown in the Table below.

#### EXAMPLES 11 AND 12

150 ml of an aqueous solution of active metals, as prepared from 35.7 g of molybdenum trioxide, 15.23  
 30 g of cobalt carbonate, 11.4 % of phosphoric acid and water, was infiltrated into 200 g of pseudo-boehmite alumina carrier ( $\text{Al}_2\text{O}_3$  content: 92.8 wt.%), which was then dried at 110°C for 5 hours. 22.4 g of tartaric acid (Example 11) or 25.2 g of malic acid (Example 12) was infiltrated into 100 g of the dried product, which was again dried at 110°C for 10 hours. Accordingly, Catalysts-K and L were obtained. Regarding the active metal contents in these catalyst samples, Mo content was 15 % by weight as  $\text{MoO}_3$ , Co content was 4 %  
 35 by weight as CoO and P content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of the tartaric acid or malic acid added was 1.25 molar times of the total molar number of Mo and Co. The activity test of these catalyst samples was effected in the same manner as in Example 1, and the results obtained are shown in the Table below.

#### 40 EXAMPLE 13

160 ml of an aqueous solution of active metals, as prepared from 38.5 g of molybdenum trioxide, 16.2 g of nickel carbonate, 12.3 g of 85 % phosphoric acid and water, was infiltrated into 200 g of the above-mentioned  $\gamma$ -alumina carrier, which was then dried at 110°C for 5 hours. Next, 67.0 g of citric acid was  
 45 infiltrated into the dried product, which was again dried at 110°C for 10 hours. Thus, a catalyst sample (Catalyst-M) was obtained. Regarding the active metal contents in Catalyst-M, Mo content was 15 % by weight as  $\text{MoO}_3$ , Ni content was 4 % by weight as NiO, and P content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of the citric acid added was 0.8 molar time of the total molar number of Mo and Ni. The activity test of the catalyst was effected in the same manner as in Example 1, and the results obtained are shown in the  
 50 Table below.

#### COMPARATIVE EXAMPLES 1 TO 4

800 ml of an aqueous solution of active metals, as prepared from 193 g of molybdenum trioxide, 82 g  
 55 of cobalt carbonate, 61.5 g of 85 % phosphoric acid and water, was infiltrated into 1 kg of the same  $\gamma$ -alumina carrier as that used in the previous examples. The thus infiltrated  $\gamma$ -alumina carrier was then dried at 110°C for 5 hours. As a complexing agent, 69.7 g of EDTA (Comparative Example 1), 59.3 g of nitrilotriacetic acid (Comparative Example 2), 96.2 g of diethylenetriamine (Comparative Example 3) or 57.2

g of ethylenediamine (Comparative Example 4) was infiltrated into 250 g of the dried product, which was again dried at 110°C. Accordingly, catalyst samples (Catalysts-N, O, P and Q) were prepared. Regarding the active metal contents in these catalyst samples, Mo content was 15 % by weight as MoO<sub>3</sub>, Co content was 4 % by weight as CoO and P content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The complexing agent added was 0.6 molar time (as EDTA), 0.8 molar time (as nitrilotriacetic acid) or 2.5 molar times (as diethylenetriamine or ethylenetriamine), respectively, of the total molar number of Mo and Co. The activity test of these catalysts was effected in the same manner as in Example 1, and the results obtained are shown in the Table below.

| Example No.           | Catalyst | Desulfurization Percentage (%) | Relative Rate Constant |
|-----------------------|----------|--------------------------------|------------------------|
| Example 1             | A        | 97.2                           | 308                    |
| Example 2             | B        | 95.7                           | 217                    |
| Example 3             | C        | 96.2                           | 240                    |
| Example 4             | D        | 95.8                           | 221                    |
| Example 5             | E        | 94.8                           | 185                    |
| Example 6             | F        | 95.4                           | 205                    |
| Example 7             | G        | 96.7                           | 284                    |
| Example 8             | H        | 95.1                           | 194                    |
| Example 9             | I        | 96.0                           | 230                    |
| Example 10            | J        | 95.3                           | 201                    |
| Example 11            | K        | 95.0                           | 191                    |
| Example 12            | L        | 95.6                           | 213                    |
| Example 13            | M        | 96.2                           | 240                    |
| Comparative Example 1 | N        | 92.3                           | 132                    |
| Comparative Example 2 | O        | 92.7                           | 138                    |
| Comparative Example 3 | P        | 91.5                           | 121                    |
| Comparative Example 4 | Q        | 89.5                           | 100                    |

In accordance with the present invention, there is provided a method of preparing a catalyst for hydrogenation of a crude hydrocarbon oil, in which a determined amount of hydroxycarboxylic acid is applied to a catalyst having metals of the Group VI and the Group VIII of the Periodic Table and optionally phosphoric acid as carried on a carrier and thereafter the catalyst is dried at a temperature not higher than 200°C prior to loading onto a reactor. The catalyst of the invention is usable for high hydrogenation of a hydrocarbon oil for deep desulfurization or denitrogenation of the same. Therefore, the catalyst may sufficiently satisfy the requirement of reducing the sulfur content in a light oil as one advantageous merit. As another merit, the method of the present invention is free from presulfurization of generating any harmful and toxic gas, and the catalyst as prepared by the method of the present invention may stably be carried on the carrier.

#### Claims

1. A method of preparing a catalyst for hydrogenation of a hydrocarbon oil, in which an hydroxycarboxylic acid is added to a catalyst comprising metals of both Groups VI and VIII of the Periodic Table on a carrier in a molar amount of from 0.3 to 5 times that of the total molar amount of the Group VI and VIII metals, characterised in that the resulting catalyst is dried at a temperature not higher than 200°C before loading onto a reactor.
2. A method of preparing a catalyst for hydrogenation of a hydrocarbon oil, in which a hydroxycarboxylic acid is added to a catalyst comprising metals of both Group VI and VIII of the Periodic Table, and

phosphoric acid on a carrier, the carboxylic acid being in molar amount of from 0.3 to 5 times that of the total metal molar amount of the Group VI and VIII, characterised in that the resulting catalyst is dried at a temperature not higher than 200 °C prior to loading onto a reactor.

- 5 3. The method as claimed in claim 1 or 2, in which the metal of Group VI of the Periodic Table is at least one of Mo and W.
4. The method as claimed in any preceding claim, in which the metal of Group VIII of the Periodic Table is at least one of Co and Ni.
- 10 5. The method as claimed in any preceding claim, in which the hydroxycarboxylic acid is one or more of glycolic acid, hydroxypropionic acid, hydroxybutyric acid, hydroxyhexanoic acid, tartaric acid, malic acid, glyceric acid, citric acid and gluconic acid.
- 15 6. The method as claimed in any preceding claim, in which the amount of the metal of Group VI carried on the carrier is from 5 to 30 % by weight, expressed as its oxide.
7. The method of preparing a catalyst as claimed in any preceding claim, in which the amount of the metal of Group VIII carried on the carrier is from 1 to 8 % by weight, as expressed as its oxide.
- 20 8. The method as claimed in claim 2, in which the phosphoric acid is one or more of meta-phosphoric acid, pyro-phosphoric acid, ortho-phosphoric acid, tri-phosphoric acid, tetraphosphoric acid and nickel phosphate.
- 25 9. The method as claimed in claims 2 or 8, in which the amount of the phosphoric acid in the catalyst is from 0.1 to 8 % by weight, expressed as  $P_2O_5$ .
10. A method of hydrogenating a hydrocarbon oil utilising a catalyst prepared in accordance with any of the preceding claims.

#### Patentansprüche

1. Verfahren zum Herstellen eines Katalysators zur Hydrierung eines Kohlenwasserstofföls, bei dem eine Hydroxycarbonsäure einem Katalysator zugegeben wird, welcher Metalle sowohl von der Gruppe VI als auch der Gruppe VIII des Periodensystems auf einem Träger in einer Molarmenge von dem 0,3 bis 5-fachen der Gesamtmolarmenge der Metalle aus den Gruppen VI und VIII aufweist, **dadurch gekennzeichnet**, daß der erhaltene Katalysator bei einer Temperatur von nicht höher als 200 °C vor dem Einbringen in einen Reaktor getrocknet wird.
- 40 2. Verfahren zur Herstellung eines Katalysators zur Hydrierung eines Kohlenwasserstofföls, bei dem eine Hydroxycarbonsäure einem Katalysator zugegeben wird, welcher Metalle sowohl von der Gruppe VI als auch der Gruppe VIII des Periodensystems und eine Phosphorsäure auf einem Träger aufweist, wobei die Carbonsäure in einer Molarmenge von dem 0,3 bis 5-fachen der Gesamtmolarmenge der Elemente der Gruppe VI und VIII vorhanden ist, **dadurch gekennzeichnet**, daß der erhaltene Katalysator bei einer Temperatur von nicht höher als 200 °C vor dem Einbringen in einen Reaktor getrocknet wird.
- 45 3. Verfahren nach Anspruch 1 oder 2, bei dem das Metall der Gruppe VI des Periodensystems wenigstens Mo und/oder W ist.
- 50 4. Verfahren nach einem der vorangehenden Ansprüche, bei dem das Metall der Gruppe VIII des Periodensystems wenigstens ein solches ist, welches aus der Gruppe gewählt ist, die Co und/oder Ni umfaßt.
- 55 5. Verfahren nach einem der vorangehenden Ansprüche, bei dem die Hydroxycarbonsäure eine oder mehrere Säuren der Gruppe aufweist, welche Glycolsäure, Hydroxypropionsäure, Hydroxybutyrsäure, Hydroxyhexansäure, Weinsäure, Hydroxybernsteinsäure, Glycerinsäure, Zitronensäure und Gluconsäure umfaßt.

6. Verfahren nach einem der vorangehenden Ansprüche, bei dem die Menge des Metalls der Gruppe VI auf dem Träger ausgedrückt als Oxyd von 5 bis 30 Gewichtsprozent ausmacht.
- 5 7. Verfahren zum Herstellen eines Katalysators nach einem der vorangehenden Ansprüche, bei dem die Menge des Metalls der Gruppe VIII auf dem Träger ausgedrückt in Oxyden von 1 bis 8 Gewichtsprozent ausmacht.
8. Verfahren nach Anspruch 2, bei dem die Phosphorsäure eine solche ist, die aus der Gruppe gewählt ist, welche eine oder mehrere von Metaphosphorsäure, Pyrophosphorsäure, Orthophosphorsäure, 10 Triphosphorsäure, Tetraphosphorsäure und Nickelposphat umfaßt.
9. Verfahren nach Anspruch 2 oder 8, bei dem die Menge der Phosphorsäure im Katalysator ausgedrückt als  $P_2O_5$  0,1 bis 8 Gewichtsprozent ausmacht.
- 15 10. Verfahren zum Hydrieren eines Kohlenwasserstofföls unter Einsatz eines Katalysators, welche gemäß einem der vorangehenden Ansprüche hergestellt ist.

### Revendications

- 20 1. Procédé pour préparer un catalyseur d'hydrogénation d'une huile hydrocarbonée, dans lequel on ajoute un acide hydroxycarboxylique à un catalyseur comprenant des métaux des deux groupes VI et VIII du Tableau Périodique sur un support en une quantité molaire égale à 0,3 à 5 fois la quantité molaire totale des métaux des groupes VI et VIII, caractérisé en ce que le catalyseur résultant est séché à une 25 température non supérieure à 200 °C avant chargement sur un réacteur.
2. Procédé pour préparer un catalyseur d'hydrogénation d'une huile hydrocarbonée, dans lequel on ajoute un acide hydroxycarboxylique à un catalyseur comprenant des métaux des deux groupes VI et VIII du Tableau Périodique, et un acide phosphorique sur un support, l'acide carboxylique étant en une 30 quantité molaire égale à 0,3 à 5 fois la quantité molaire totale des métaux des groupes VI et VIII, caractérisé en ce que le catalyseur résultant est séché à une température non supérieure à 200 °C avant chargement sur un réacteur.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel le métal du groupe VI du Tableau Périodique est au moins l'un de Mo et de W.
- 35 4. Procédé selon l'une des revendications précédentes, dans lequel le métal du groupe VIII du Tableau Périodique est au moins l'un de Co et de Ni.
5. Procédé selon l'une des revendications précédentes, dans lequel l'acide hydroxycarboxylique est l'un ou plusieurs des suivants : acide glycolique, acide hydroxypropionique, acide hydroxybutyrique, acide 40 hydroxyhexanoïque, acide tartarique, acide malique, acide glycérique, acide citrique et acide gluconique.
6. Procédé selon l'une des revendications précédentes, dans lequel la quantité du métal du groupe VI porté sur le support est égale à 5 à 30% en poids, exprimée en tant que son oxyde.
- 45 7. Procédé pour préparer un catalyseur selon l'une des revendications précédentes, dans lequel la quantité du métal du groupe VIII portée sur le support est égale à 1 à 8% en poids, exprimée en tant que son oxyde.
- 50 8. Procédé selon la revendication 2, dans lequel l'acide phosphorique est l'un ou plusieurs des suivants : acide métaphosphorique, acide pyrophosphorique, acide orthophosphorique, acide triphosphorique, acide tétraphosphorique et phosphate de nickel.
- 55 9. Procédé selon la revendication 2 ou la revendication 8, dans lequel la quantité d'acide phosphorique dans le catalyseur est égale à 0,1 à 8% en poids, exprimée en tant que  $P_2O_5$ .



10. Procédé d'hydrogénation d'une huile hydrocarbonée utilisant un catalyseur préparé selon l'une quelconque des revendications précédentes.

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